Polysaccharide Blend Fibres Formed from NaOH, N-Methylmorpholine-N-oxide and 1-Ethyl-3-methylimidazolium acetate

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Abstract
The aim of the study was to find new structured biopolymer blends bearing adjustable properties able to produce innovative materials. Apart from cellulose and three solvents (NaOH, N-methylmorpholine-N-oxide [NMMO] and 1-ethyl-3-methylimidazolium acetate [EMIMac]), 15 different polysaccharides were chosen to study the interactions of polysaccharides or their mixtures in solutions, as well as the solid state after forming. Dissolution screenings yielded promising polysaccharides, which were used for the preparation of cellulose/ polysaccharide solutions and subsequently for the shaping of blends with cellulose. The solubility and miscibility were evaluated by microscopy, DSC, particle analysis and rheology. Polysaccharides with a structure similar to that of cellulose, e.g., xylan, carrageenan or cellulose carbamate were not miscible, showing globular morphologies, whereas high-molar and side chains containing polysaccharides such as xanthan or tragacanth gum form co-continuous morphologies. The forming of blend fibres was nevertheless possible for all three solvents. The textile-physical properties of the blend fibres were slightly decreased compared to those of the unmodified fibre, in which fibres from NMMO and EMIMac had the highest performance. The presence of blended polysaccharides in the fibres produced was verified by residue sugar analysis, in which the highest amounts occurred for EMIMac fibres.

Key words: *polymer blends, polysaccharides, cellulose solvents, ionic liquids, cellulosic fibre, calorimetry, rheology.*

Introduction

Multicomponent systems (polymer blends, alloys, composites, interpenetrating networks) are receiving more and more attention owing to their scientific interest and practical applications. The production of complex materials is connected with knowledge of the interactions between components from a structural, thermodynamic and kinetic point of view. Therefore, it is necessary to consider the molecular-structural peculiarities which determine both the phase diagram (monophase or multiphase systems) and kinetics associated with reaching thermodynamic equilibrium [1].

Cellulose materials offer several advantages when combined with plastics due to their low density, high modulus, strength, high stiffness, little damage during processing, few requirements concerning processing equipment, biodegradability and relatively low price [2, 3]. Hydrogen bonding between -OH groups are recognised as an important factor in providing driving forces for the attainment of thermodynamic miscibility in many polyblend systems where polysaccharides are present [4]. There exist two ways of producing blends where one of the components is a polysaccharide: mixing the polymers in a softened or molten state, or the blending of the components from their solutions. Using the first method, problems occur due to incompatibility between the hydrophilic cellulose fibres and hydrophobic thermoplastic matrix [5]. The second way is attractive since the existence of a variety of solvent systems opens the way for the systematic preparation of miscible cellulosic/ synthetic polymer blends, which is possible because cellulose solvents can also dissolve many synthetic polymers [1]. Considerable effort has been devoted to the preparation of compatible or miscible blends of cellulose with polyamides [6], polyesters [7], polyethers [8], vinyl polymers [9] and other polysaccharides [10]. Investigations of mixtures of cellulose and polyacrylonitrile were performed in an ionic liquid - BMIMCl [11]. The blend fibres spun showed very interesting properties concerning enhanced elongation, reduction of fibrillation tendency and improved dyeing behaviour.

The aim of this paper is to report the results of the common research project called "Polysaccharide-polysaccharide

Abbreviations

Alginic acid	- Alginic acid sodium salt
BMIMCl	- 1-Butyl-3-methylimidazolium chloride
CC	- Cellulose carbamate
CMC	- Carboxymethylcellulose
CMX	- Carboxymethylxylan
DP	- Degree of polymerisation
EMIMac	- 1-Ethyl-3-methylimidazolium acetate
LBG	- Locust bean gum
MHEC	- Methylhydroxyethylcellulose
NMMO	- *N*-Methylmorpholine-*N*-oxide monohydrate
Starch	- Starch, cationized

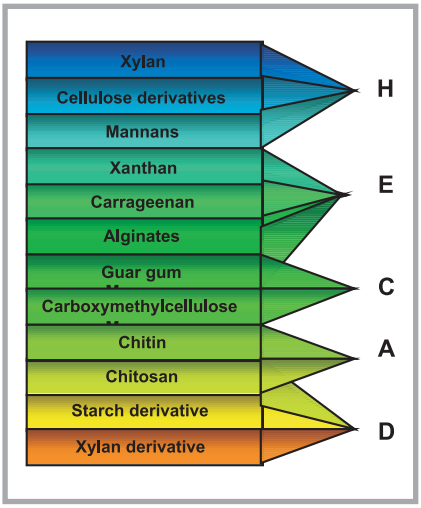

Figure 1. *Desired effects of blended polysaccharides on cellulose properties; H - hydrophilicity / hydrophobicity, E - elasticity, C - charge (surface), A - antimicrobial activity, D - dyeability.*

assemblies and the development of polysaccharide re-assemblies" within the European Polysaccharide Network (EPNOE). In this study, 15 different polysaccharides were chosen to be mixed with cellulose, after which their solution properties and fibre spinning behaviour were studied. The various polysaccharides were chosen to produce different properties, as shown in (***Figure 1***). By studying the structure-property-relations with a variety of analytical methods, new possibilities for the design of interesting cellulose-based fibre materials will be created.

Besides cellulose, the research focused on a selection of promising polysaccharides, mixtures of cellulose with polysaccharides, variations of solvents and the shaping of polysaccharide blends. Three solvent methods of dissolving were followed:

(i) sodium hydroxide-water (called NaOH),
(ii) *N*-methylmorpholine-*N*-oxide monohydrate (called NMMO) and
(iii) ionic liquids.

Although the NaOH dissolving process is scientifically well-advanced, it can still only be conducted on a lab-scale [12]. NMMO is industrially used for man-made fibres (Lyocell technology) to the amount of ca. 140.000 tons per year [13, 14]. Ionic liquids, especially imidazolium salts, exhibit a promising alternative to overcome the restrictions of NMMO regarding limited dissolution behaviour and thermal stability [15 - 17].

Experimental

Reagents

N-methylmorpholine-*N*-oxide (NMMO with 50.4% water (v/v) solution) and 1-ethyl-3-methyl-imidazolium acetate (EMIMac) were obtained from BASF (Ludwigshafen, Germany). EMIMac purity was a minimum of 95% and was used as supplied. For NaOH spinning, a 10.2% NaOH (v/v) solution containing 1.3 wt.% of ZnO was used. The cellulose was a bleached spruce sulfite pulp characterised by the following data: content of α-cellulose = 90.6%, DP 495, carboxyl groups = 6.9 µmol/g, carbonyl groups = 48.3 µmol/g, and moisture = 7.5%. For the preparation of NaOH solutions, cellulose from spruce was used (DP 641), which was subjected to enzymatic modification, decreasing the DP to 370 [18, 19]. Caustic soda and propyl gallate were applied as stabilisers in the NMMO and EMIMac fibre production. The following polysaccharides were used: derivatives of cellulose (cellulose carbamate, carboxymethylcellulose, methylhydroxyethylcellulose), mannans (guar gum, locust bean gum, tragacanth gum), hemicelluloses (xylan, carboxymethylxylan), chitosan, chitin, starch (cationized), ι-carrageenan, alginic acid sodium salt and xanthan. Special available properties of the polysaccharides are summarised in ***Table 1***.

Preparation of polysaccharide solutions

NMMO and *EMIMac*: 227 g of 50% (v/v) NMMO or 75% (v/v) EMIMac, respectively, and 13.8 g to 30.6 g of pure cellulose (i.e. 9 % to 20 % in the final solution) or mixtures of cellulose and one polysaccharide (with ratio varying from 100 / 0 to 0 / 100) were weighed in a laboratory reactor. After stirring the mixture for 15 min at room temperature, the reactor was connected to a rotary evaporator (appr. 30 mbar), and the temperature of the reactor was then raised to 90 °C gradually. A solution was obtained after stirring for 240 min and immediately subjected to measurements. The final water content in the NMMO solutions was 13.3 wt.%, which corresponds to the monohydrate of NMMO.

NaOH: The cellulose pulp of 75% water was placed in a mixing tank equipped with a high-speed agitator and cooling jacket, and the NaOH/ZnO solution was

Table 1. *Properties of the polysaccharides;* Laboratory sample.*

Polysaccharide	Distributor	Dry matter	Properties avalaible	
Cellulose carbamate	*	52.2	DP (cuox): DS: Nitrogen content:	266 0.37 2.88%
Carboxymethylcellulose	ROTH 3333.2	90.0	Content: Sodium glycolal: Salt residue: Sulfate ash: pH-value: DS: Sodium:	> 99,5% < 0.4% < 0.5% (NaCl + Na glycolat) 20 – 30% 6 – 8 0.65 – 0.85% 6.5 – 9.5%
Methylhydroxyethylcellulose	WOLFF 4861.2	96.5		
Guar gum	*	88.1		
Locust bean gum	*	87.6		
Tragacanth gum	*	89.6	Nitrogen content:	
Xylan	ROTH 7500.1	97.4	M: DP: Sulfate ash:	13700 g/mol 100 - 104 ≤ 10%
Carboxymethylxylan	*	86.6	DS	1.11
Chitosan	DALWOO	89.6	M: Degree of deacetylation: Protein content: Residue on Ignition:	5000 g/mol 86% 0.19% 0.28%
Chitosan	NOVASSO OY	86.3	M: Degree of deacetylation:	400 000 – 500 000 g/mol 78-82%
Chitin	ROTH 8845.2	95.0	M:	400.000 g/mol
Starch, cationised	*	86.0	DS: pH-value: Nitrogen content	0,04 3 – 6 0,70 ± 0,06
ι-Carrageenan	FLUKA 22045	88.3	Sulphur:	8,21%
Alginic acid sodium salt	ROTH 9180.2	87.1	Ash: pH-value:	18 – 27% (600°C) 5,5 – 7,5
Xanthan	*	88.8		

added. The process was completed after 60 minutes at a temperature ranging from -2 to +5 °C. The total cellulose content in the solution was 6 wt.%, and 2.5, 10 or 20 wt.% with respect to cellulose for the blended polysaccharide, where the total NaOH content was 7.8 wt.%. For the preliminary tests of solubility, 2 g of polysaccharide was introduced to 10 g of water at a temperature of 20 °C, mixed with 10 g of 18 wt.% NaOH and then stored for 24 h at room temperature.

Differential scanning calorimetry (DSC)

The solutions were measured on a Mettler Toledo DSC 822e device at a heating rate of 10 °C/min from room temperature up to 500 °C in a nitrogen atmosphere.

Particle analysis

Particle size distribution was measured by the laser diffraction method using a HELOS, type BF (Sympatec GmbH, Clausthal, Germany) with a He-Ne-laser at a wavelength of 633 nm maintained at a temperature of 85 °C.

Rheology

NMMO: Steady state (cone/plate geometry 4°, 40 mm) and oscillatory shear experiments were made on the solutions using a stress-controlled Bohlin Gemini rheometer (Malvern Instruments Ltd., Malvern, UK) equipped with a Peltier temperature control system heated to 90 °C. *EMIMac*: The zero-shear viscosity, loss and storage modules were measured using a THERMO-HAAKE rheometer (Karlsruhe, Germany) with a temperature controllable cone/plate and plate/plate-sensor of different size, which enabled sample shearing both in the rotational as well as oscillating operating modes. There were corresponding software (Rheowin, Rheosoft) readouts of the discrete measuring parameters, master curves and calculated spectra. *NaOH*: A rheological study was carried out using a Brookfield DV-II+Pro viscometer (Brookfield Viscometers Ltd., Essex, UK) equipped with Rheocalc software.

Optical microscopy observations

NMMO: Experiments were carried out in the transmission mode and between cross polarisers with a Leika DM 4500 equipped with a 3-CCD JVC camera and Linkam hot stage heated to 90 °C. Image analysis was performed by means of Areas® software, developed by Microvision. *EMIMac:* A binocular microscope (Axiolab, Carl Zeiss Jena, Germany) with polarisation, compensation, phase contrast, various filters and a magnification of up to 500 : 1 was used.

Scanning electron microscopy observations

The samples were observed using a Philips FEI XL30 ESEM with a LaB6 gun in the environmental mode (~ 5 mbar, 15 keV, 4 °C), preserving humidity and preventing drying, which could induce modifications of the samples (pore or cavity closure and plastic deformation).

Spinning trials

EMIMac and NMMO: Both fibre types were spun on self-made piston spinning equipment, which is described in detail in ref. [20].

NaOH: By means of an experimental wet spinning machine, the spinning solution was pressed into a coagulation bath containing 100 g/L of H_2SO_4 and 150 g/L of Na_2SO_4 at a temperature of 17 °C. The fibres spun were drawn (R_{max} = 30%) in water at 85 °C, rinsed with water at 40 °C, passed through a finishing solution containing 7 g/L of Berol Fintex, dried on cylinders at 85 to 90 °C and finally tension-collected on spools as multifilament yarn. The take-up speed applied was 30 m/min.

Fibre characterisation

Determination of the water retention values of the cellulose fibres was carried out according to DIN 53814. The textile-physical fibre parameters were determined according to the following methods: the fineness according to DIN EN ISO 1973, tenacity and elongation - DIN EN ISO 5079 and loop tenacity - DIN 53843, part 2.

Uptake experiments

To determine the uptake of the polysaccharide blend into cellulose fibre, the concentrations of sugars (arabinose, galactose, mannose, xylose, glucose) in the polysaccharide blend, the pure cellulose fibre (blank) and the blended fibre were measured. Sugar analysis of the fibres was carried out by way of two-step H_2SO_4 hydrolysis and borate anion exchange chromatography. The uptake U in % is calculated by equation (1), where c is the sugar concentration in the polysaccharide blended fibre in %, b the sugar concentration in the pure cellulose fibre in %, and s is the sugar concentration in the polysaccharide blend. Afterwards the uptake is normalised to an uptake ration V in % by way of equation (2), using the content of the polysaccharide blend in the fibre (f). Thereby a comparison between different fibre types of varying concentration ratio is possible.

$$U = \frac{(c-b)}{s} \cdot 100\% \quad (1)$$

$$V = \frac{U}{f} \cdot 100\% \quad (2)$$

For analysis of CMC uptake ration, fibres were hydrolysed with perchloric acid, and the eight building blocks of CMC were analysed by size exclusion chromatography with pulsed amperometric detection (AEC-PAD, Dionex Corp.), according to Horner et al. [21]. Starch uptake rates were analysed enzymatically. The material was digested with amylase and amyloglucosidase according to Rademacher et al. [22].

Results and discussion

Dissolution screenings

Before the preparation of blends with cellulose, the dissolution of the various polysaccharide samples in solvents NaOH, EMIMac and NMMO was studied. Dissolution screenings of the 15 polysaccharides were carried out to select the best soluble ones. The polysaccharide concentrations chosen varied from 1 – 25%. Results are displayed in ***Table 2*** (see page 24), classified in four classes: highly soluble, partly soluble, not soluble but with low swelling and not soluble.

The chitin and chitosan samples were not soluble in any of the three solvents. Comparable dissolution succeeded in the case of CMC, CC, xylan, xanthan and the mannans, guar gum, LBG and tragacanth gum. These similarities are very useful for subsequent fibre spinning by means of the three solvents and for comparing the forming behaviour and properties of the fibre species. The total differences concerned MHEC, starch, carrageenan, alginic acid and CMX, confirming the different chemical nature of the solvents. Contrary to NaOH and NMMO, EMIMac ionic liquid is not able to dissolve polysaccharides with functional groups like carrageenan or MHEC below about only 1%. Moreo-

Table 2. *Dissolution screening of polysaccharides: (+) highly soluble, (+/–) partly soluble, (–) not soluble but with low swelling, (– –) not soluble.*

Polysaccharide	EMIMac	NaOH	NMMO
Carboxymethylcellulose	+	+/-	+/-
Methylhydroxyethylcellulose	-	+/-	+/-
Cellulose carbamate	+	+/-	+
Chitosan, (M = 5.000)	- -	- -	-
Chitosan, (M = 500.000)	- -	- -	-
Chitin	- -	- -	-
Starch, cationized	+	+/-	- -
ι-Carrageenan	-	+/-	+
Alginic acid sodium salt	-	+/-	- -
Xylan	+	+	+
Carboxymethylxylan	+	+/-	-
Xanthan	+	+	+
Guar gum	+	+	+/-
Locust bean gum	+	+/-	+/-
Gum tragacanth	+	+/-	+

ver, this raises a question concerning the obviously better dissolution power of NaOH: whether a certain DP reduction can be calculated. Here, further investigations are necessary.

Blend fibres were prepared by mixing cellulose and another polysaccharide in a simultaneous forming process using two possibilities: collective dissolution of the polysaccharides in one solution or mixing two solutions, each containing one polysaccharide, which is described in more detail in the next chapters.

Polysaccharide blends in NaOH

The first step of the study involved the preparation of polysaccharide solutions with a concentration of 10%. It was found that xylan, xanthan and guar gum are soluble, whereas chitin and the chitosans only form suspensions. The other polysaccharides were partly soluble (***Table 2***). Consequently, the second step focused on the partly soluble polysaccharides, applying special conditions, such as lower polymer content and different temperatures during the dissolving process. Usage of approx. 6% cellulose solutions and additional polysaccharide with ratios of 9.5 : 0.5 to 8 : 2 resulted in the preparation of blend solutions with carrageenan, CC, CMC and starch. Additional cellulose/polysaccharide blends were produced with xanthan, gum tragacanth and LBG. Here, it should be mentioned that the latter polysaccharides were dissolved separately, and the two solutions were mixed.

The solutions were investigated by particle analysis (***Figure 2***). Carrageenan, CC, CMC, starch and gum tragacanth and cellulose gave a clear solution, whereas xanthan and LBG formed gel particles when mixed with cellulose, indicating part phase separation. The particle spectrum of the xanthan solution shows a wider distribution compared to that of tragacanth. This behaviour was confirmed by DSC analysis (***Figure 3***), where the curve of the cellulose/xanthan solution possesses upstreaming peaks before reaching the main endothermic one, indicating lower miscibility. Consequently, the spinning of cellulose with xanthan and LBG brought some difficulties, as described later.

Surprisingly, the zero shear viscosity of the pure cellulose solutions is reduced by addition of a second polysaccharide. This behaviour is similar to that of NMMO solutions but opposite to that of blend solutions of EMIMac, as summarised for selected cellulose/blend polysaccharide solutions in ***Table 3***. ***Figure 4*** displays the flow curves of a pure cellulose solution compared to those of cellulose/tragacanth and cellulose/xanthan solutions. It should be mentioned that the viscosities of NaOH solutions are somewhat lower compared to NMMO and EMIMac.

Polysaccharides blends in EMIMac

Ionic liquids possess extraordinary dissolution strength no matter if the polysaccharide is dissolved solely or in combination with cellulose. Xanthan, LBG, guar gum, CMC, CC, gum tragacanth, CMX, xylan and starch present good solubility in EMIMac (***Table 2***) and, consequently, were used for subsequent trials. MHEC, alginic acid and carrageenan are also

Table 3. *Zero shear viscosity (in Pa s) of pure cellulose and blend solutions. EMIMac, NMMO: 20% cellulose, 2.5% blend polysaccharide*; NaOH: 6% cellulose, 2.5% blend polysaccharide* except for carrageenan 10%*; * - with respect to cellulose.*

Polysaccharide blend	Solvent		
	NaOH	EMIMac	NMMO
-	12.5	10780	12730
Xanthan	6.0	20020	10630
Tragacanth gum	5.5	-	9933
Carrageenan	5.1	-	10650
LBG	5.5	14070	-

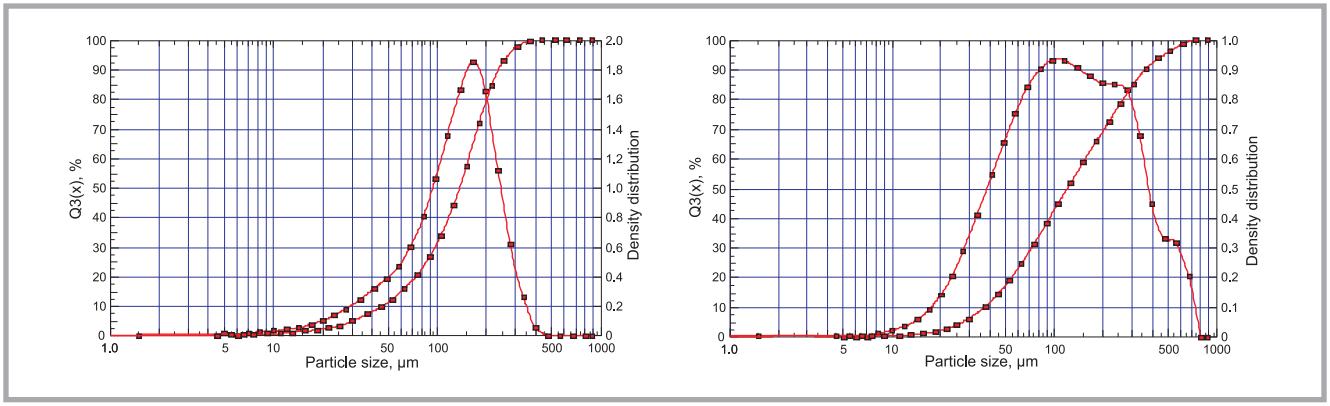

Figure 2. *Particle analysis (sum and density distribution) of a cellulose/tragacanth gum solution (97.5 : 2.5; left) and cellulose/xanthan solution (97.5 : 2.5; right), each in NaOH.*

partly soluble, but only up to a concentration of 1%. The rheological behaviour of the solution was investigated to evaluate the influence of an additional polysaccharide as compared to pure cellulose solution (***Table 4***, see page 26). The blend solutions exhibit higher viscosities and enhanced elasticity, esp. of xanthan, gum tragacanth and LBG. ***Figure 5*** shows the evolution of the storage (G`) and loss (G``) modulus versus the pulsation (rad/s) for a solution of cellulose/LBG compared to the pure cellulose solution. The storage modulus at the crossover point is enhanced, which is connected with the higher elasticity. In the case of xanthan, the side chains containing glucuronic acid and *O*-acetylmannose cause diminished flexibility due to lower interactions with the cellulose. In fact, the crossover point is enhanced, indicating definitely improved elasticity of the blend solution.

DSC thermograms of the solely dissolved polysaccharide as well as of the cellulose/polysaccharide mixtures were conducted to evaluate the miscibility of cellulose with the blended polysaccharide. The DSC curves were compared with those for pure solvent. As the solvent degrades from ca. 180 °C, a second heating after cooling does not reveal further information. For evaluation of the miscibility, a degradation peak of 180 – 250 °C was used. Whereas xanthan, CMC, CC, CMX, xylan and starch show moderate miscibility with cellulose, gum tragacanth, guar gum and LBG are different. As an example, the curves of gum tragacanth in comparison to those of cellulose/gum tragacanth solution in EMIMac are displayed in ***Figure 6*** (see page 26). Up to 10% of the polymer blend gives good solubility, whereas the mixed solution shows a shoulder before reaching a peak, indicating incomplete solubility. The high molecular weight of gum tragacanth (ca. 800.000 g/mol) can be the reason for these inhomogeneities, although the solution contains only ca. 0.5% of the polysaccharide blend. This result is confirmed by the microscopic investigations described later.

To evaluate the states of solutions, microscopic images were taken between cross polarisers at room temperature. Most of the pure polysaccharide solutions were bright and clear. Interestingly, only one polysaccharide solution – cellulose carbamate (15%) – showed anisotropic behaviour, which is of special importance

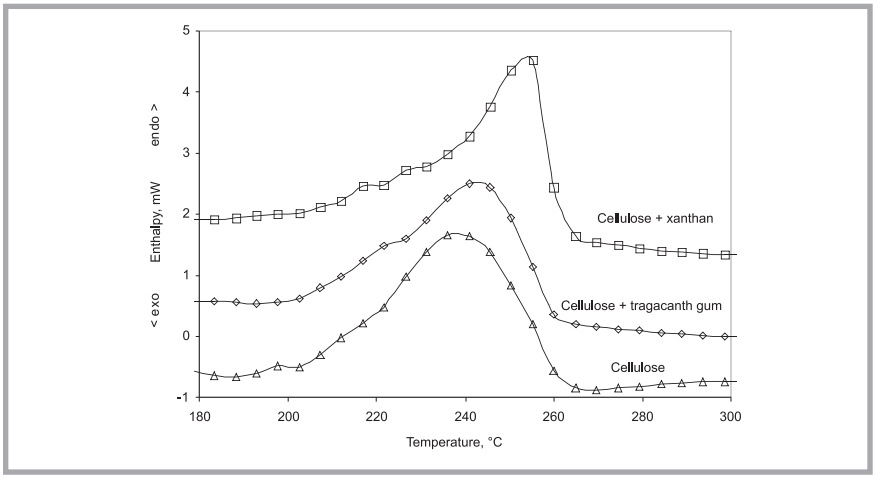

Figure 3. *DSC curves of cellulose/xanthan (97.5/2.5), cellulose/tragacanth gum (97.5/ 2.5) and pure cellulose solutions in NaOH (Enthalpy normalised).*

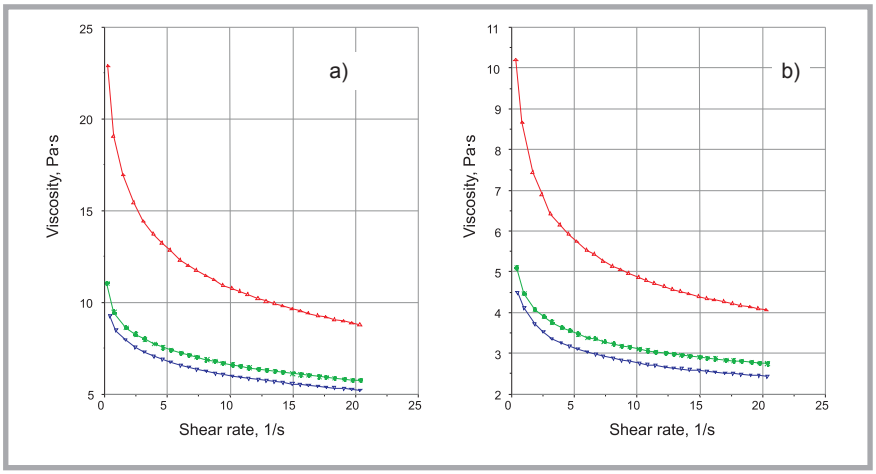

Figure 4. *Relationship between the steady-state viscosity and shear rate (flow curves) of cellulose solutions in NaOH at 10 °C (left) and 30 °C (right): pure cellulose (red), cellulose/tragacanth (green) and cellulose/xanthan (blue).*

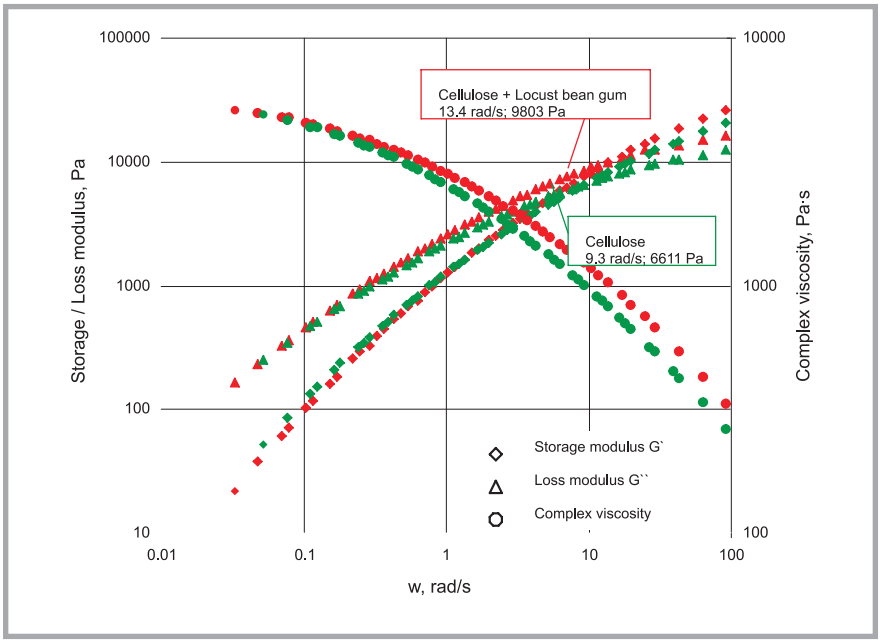

Figure 5. *Graphs of the storage (G`) and loss (G``) modulus as well as the zero shear viscosity for a solution of cellulose with locust bean gum compared to a pure cellulose solution.*

Table 4. *Rheological behaviour of cellulose solutions in EMIMac modified with different polysaccharides.*

Parameter	unit	Trial			
		VR070401	VR070641	VR070702	V20S
Cellulose	%	20	20	20	20
Second polymer		Xanthan	Xanthan	LBG	-
Mass relation cellulose : second polymer		95 / 5	97.5 / 2.5	97.5 / 2.5	
Solid content	%	20.9	20.6	20.3	19.8
Zero shear viscosity (85°C)	Pas	21430	20020	14070	10780
Reference temperature of master curves	°C	95	95	95	95
Shear rate (crossover point)	rad/s	5.74	8.0	13.4	9.3
Storage module (crossover point)	Pa	8305	8553	9803	6611
Plateau module	Pa	30840	28200	26270	20660
Unevenness (rheological)		4.0	4.1	4.3	4.6
Relaxation time λ_m bei H^*_m	s	2.9	2.2	1.3	2.9
Frequency H^*_m bei λ_m	Pas	1965	1452	941	994
Rel. Frequency H* bei λ ~ 85 s	%	22	15	22	27

for the direct forming of carbamate in ionic liquids [23]. In the case of combinations with cellulose, xanthan, tragacanth gum and LBG, anisotropic structures could be found, as shown in ***Figure 7***. This behaviour was described in analogy to cellulose solutions in NMMO and BMIMCl produced in TITK [24], which had already been discussed as liquid crystalline by different working groups [25, 26]. Cellulose solutions in NMMO with a polymer concentration higher than 20% and molar ratios of water/NMMO lower than 1 were usually found to be anisotropic. In this study, a cellulose concentration of approx. 20% with a cellulose/blend polysaccharide ratio of 97.5/2.5 for xanthan and tragacanth gum was used. LBG shows this behaviour even at ratio of 95/5. Unexpectedly, solutions of only 9% cellulose with LBG also have an anisotropic optical aspect.

It should be pointed out that inhomogeneities may arise for several reasons, such as the formation of undissolved parts, micro phase separation (depending on the concentration), the DP of the cellulose, and the water content. However, the interaction among molecules becomes weaker as the temperature increases, potentially eliminating the anisotropy of molecules. To characterise the solutions more precisely, viscosity measurements were conducted at different temperatures at a constant shear rate (***Figure 8*** of 0.5 s^{-1}, according to ref. [24]. Generally, there is a linear dependence of the viscosity on temperature, as shown by the Arrhenius plot. The change in the slope at the crossover represents the change in flow activation energy, indicating a phase transition from the anisotropic to isotropic. The cellulose/xanthan blend solution investigated shows a phase change at a temperature of 95 °C.

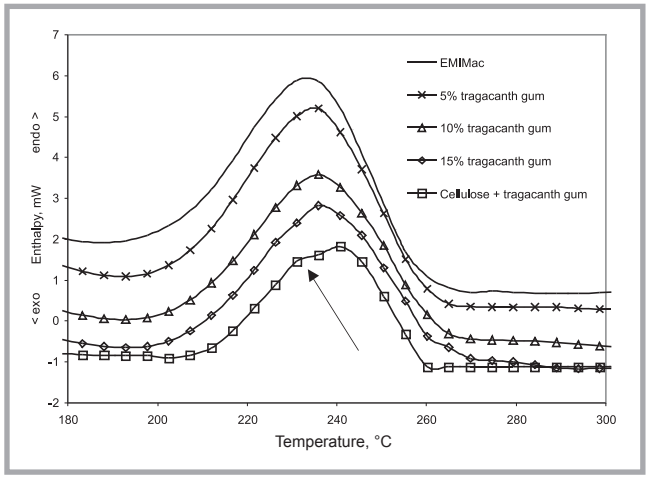

Figure 6. *Comparison of the DSC curves of tragacanth gum solutions in EMIMac and those of pure EMIMac and cellulose/gum tragacanth solution (97.5/2.5). Enthalpy normalised.*

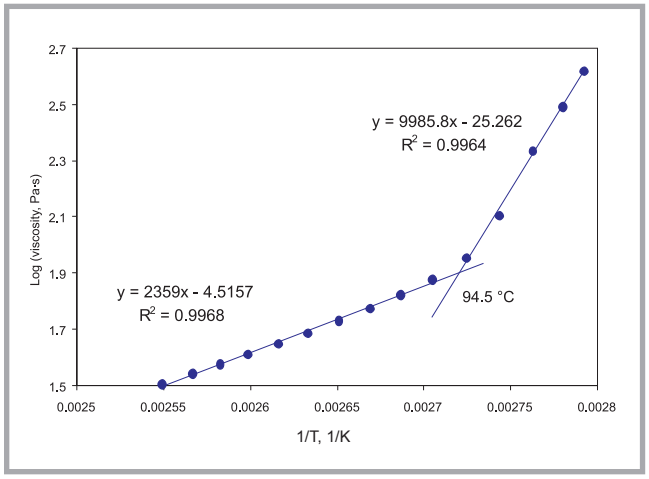

Figure 8. *Viscosity measurement of a cellulose/xanthan solution (95/5) for different temperatures at a shear rate of 0.5 s^{-1} (Arrhenius plot).*

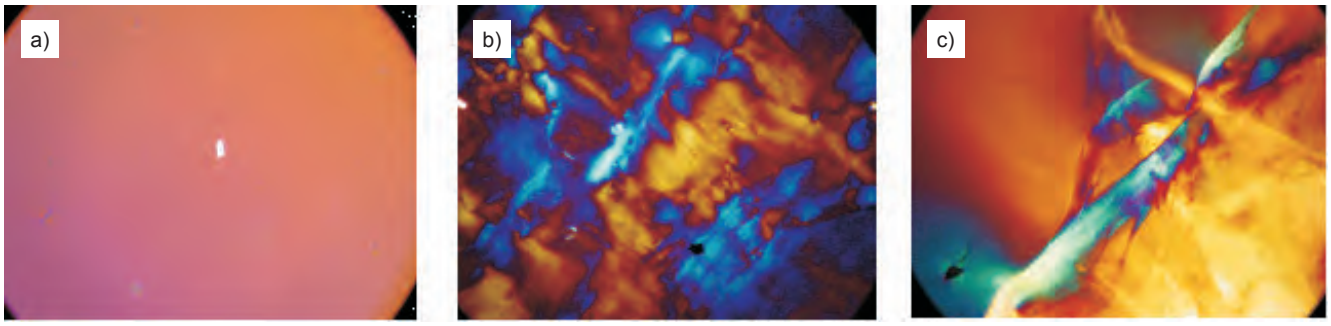

Figure 7. *Microscopic images of cellulose/blend polysaccharide solutions in EMIMac: a) cellulose/ LBG (97.5/2.5), b) cellulose/ LBG (95/5), and c) cellulose/tragacanth gum (95/5).*

Polysaccharide blends in NMMO

After dissolution screening in NMMO, the focus of the investigations was on the most soluble polysaccharides in NMMO: xylan, xanthan, carrageenan, and tragacanth gum (***Table 1***). The amount of residual undissolved polysaccharide as a function of the additional polysaccharide type was evaluated by means of optical microscopy observations. The quality of dissolution rises in the following order: tragacanth gum < xanthan, carrageenan < xylan. Solutions of cellulose with the addition of another polysaccharide at a constant total concentration of 10% were also prepared to study the blend morphology. Two types of blends providing very different morphologies were found: cellulose/xylan and cellulose/xanthan [27]. ***Figure 9*** (see page 27) represents cellulose/xylan solutions and reveals the presence of particles of xylan in the range of 2 – 4 µm, suggesting immiscibility with cellulose. The amount of particles rises with increasing xylan concentration and was estimated by image analysis to be 6.4% (***Figure 9.a***) at a cellulose/xylan ratio of 25/75. This result is close to the stated value of 7.5% in the solution and confirms that these particles are effectively xylan. However, it should be stated that xylan particles are still present at a cellulose/xylan ratio of 0/100 (***Figure 9.d***), meaning that the presence of these particles is not due to the immiscibility between xylan and cellulose chains but is a result of the interaction of xylan with the NMMO monohydrate. A possible explanation for the formation of xylan particles observed is the hydrophobic character of xylan chains, which is related to the amount of side chains, such as arabinose [28], which can cause the aggregation of the chains in aqueous solvent, such as NMMO monohydrate. In comparison, cellulose/xanthan solutions reveal a continuous phase for all

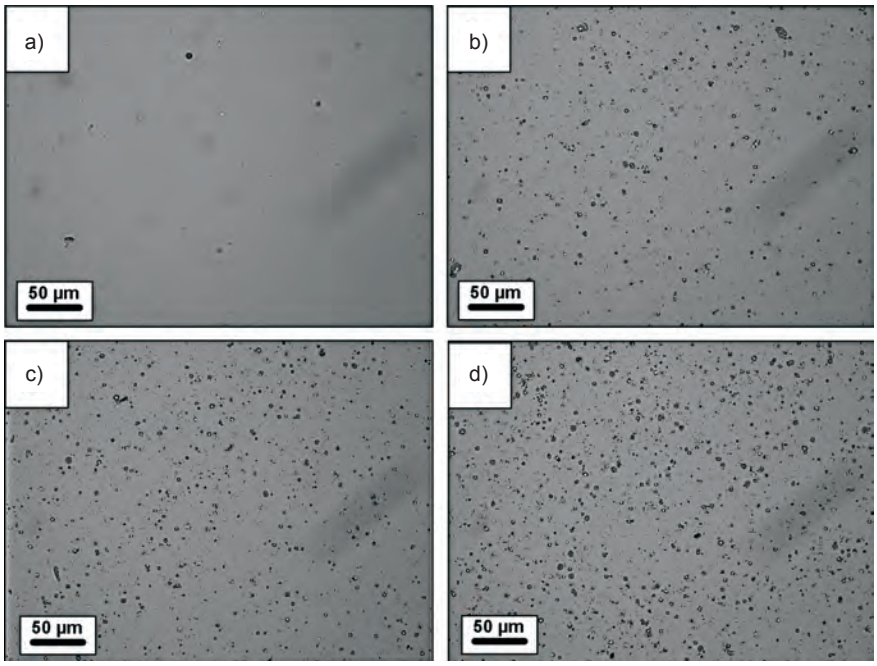

Figure 9. *Microscopic images of cellulose/xylan solutions at 90 °C with a concentration ratio of 75/25 (a) and 50/50 (b), 25/75 (c), 0/100 (d) after image analysing (xylan particles are surrounded).*

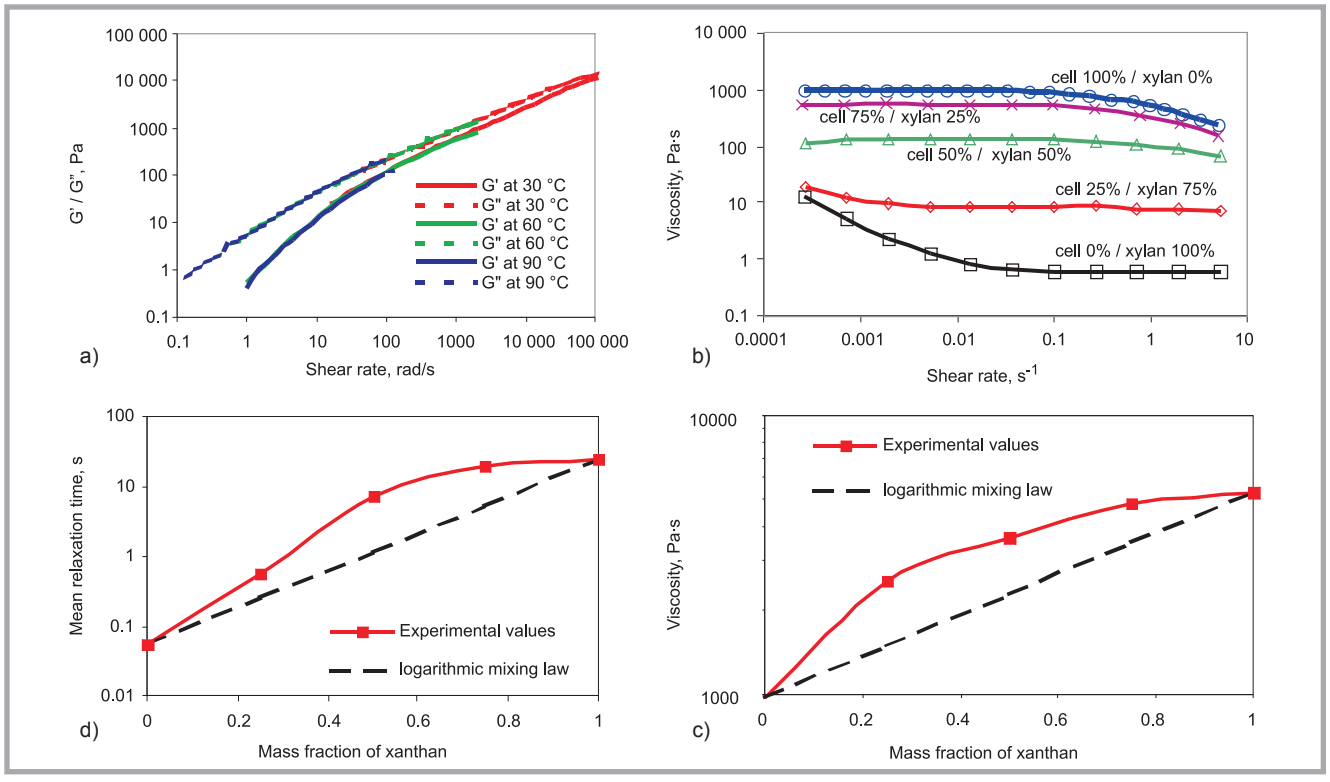

Figure 10. *Master curves of the G'& G"modulus versus pulsation at 90 °C for: a) - a cellulose/xylan (25/75) solution, b) - viscosity versus shear rate at 90 °C for different cellulose/xylan ratios, c) - relation of the zero shear viscosity to mass fraction of xanthan at 90 °C and d) - relation of relaxation time to mass fraction of xanthan at 90 °C*

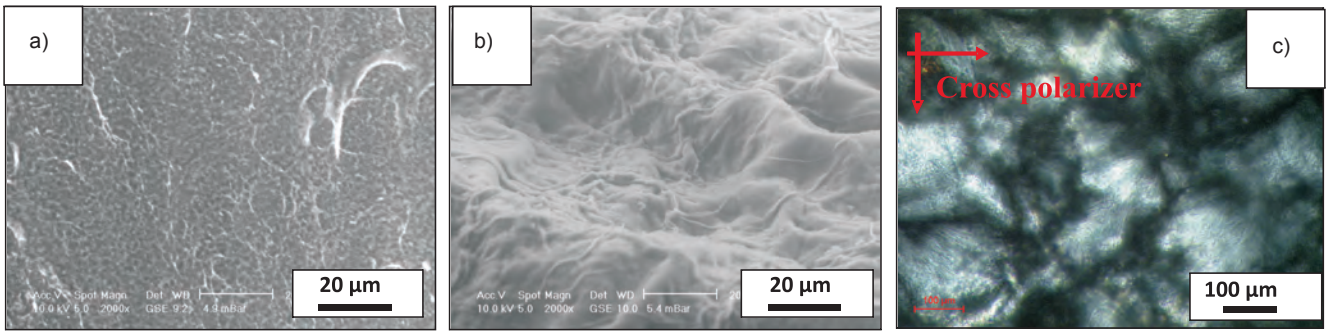

Figure 11. *Scanning electron microscopy observations of (a) a regenerated cellulose/xylan (25/75) blend and (b) a cellulose/xanthan (25/75) blend after regeneration in water at ambient temperature. Optical microscopy observation in light transmission between cross polarisers of a thin slice of a regenerated cellulose/xanthan blend (50/50) (c).*

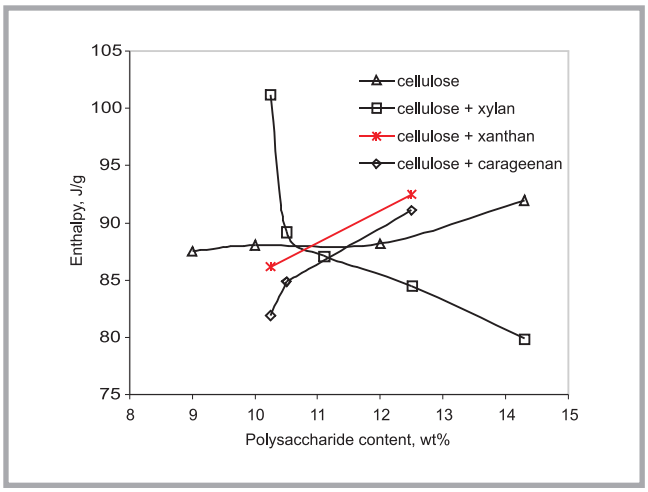

Figure 12. *Relationship between the NMMO enthalpy and concentration of polysaccharides for different cellulose / polysaccharides / NMMO solutions determined by DSC.*

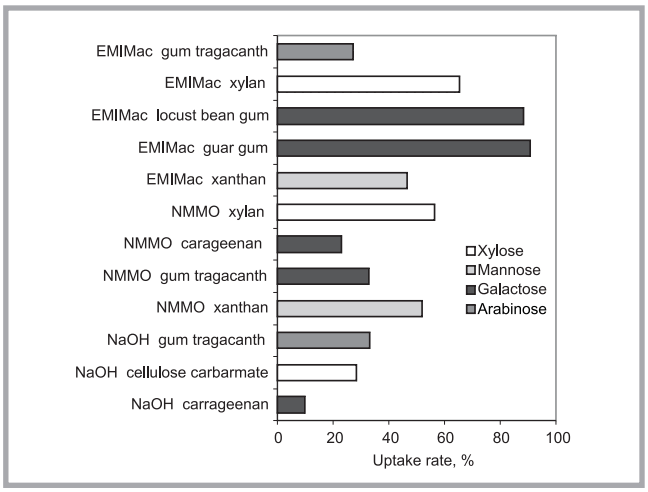

Figure 13. *Uptake rations of sugars for different fibre types.*

concentration ratios. It was not possible to distinguish the xanthan phase from the cellulose one in the solutions.

Rheological investigations of cellulose/xylan solutions revealed master curves of G' and G" for ratios from 100/0 to 50/50 that are typical for cellulose/NMMO solutions. For a ratio of 25/75, i.e. 2.5% of cellulose and 7.5% of xylan in the solution, no crossover of the G' & G" curves can be observed (***Figure 10.a,*** see page 27), which is also the case for a 2.5% cellulose/NMMO solution, where the concentration of cellulose is too low to involve the entanglement of the chains. Consequently, the addition of xylan does not change the general behaviour of the solution, meaning that no entanglements or interactions occur between cellulose and xylan chains. This is confirmed by the decay of zero shear viscosity (***Figure 10.b***), accompanied by a decreasing relaxation time with an increasing amount of xylan. Thus, in accordance with microscopic observations, cellulose/xylan blends show a globular morphology with xylan particles in a continuous phase of cellulose/NMMO for all blend ratios. The regeneration of cellulose/xylan blends leads to the same type of morphology with particles of xylan in a continuous phase of cellulose, as revealed by the degradation caused by an electron beam, which was observed by scanning electron microscopy; xylan chains degrade much faster than cellulose ones (***Figure 11.a***). The rheological study of cellulose/xanthan solutions shows an inverse phenomenon when compared to xylan, exhibiting a large increase in the zero shear viscosity and relaxation time (***Figures 10.c*** and ***10.d***). This behaviour is mainly due to the high molar mass of xanthan chains (up to 2 million) and the hydrogen bond interactions occurring between the chains, which also favour immiscibility with the cellulose chains. However, hydrogen bonding between OH groups of cellulose and xanthan chains might also occur. As shown in ***Figure 11.b***, the regeneration of cellulose/xanthan blends leads to a co-continuous morphology with regenerated cellulose surrounded by a network of xanthan, which is confirmed by the microscopic observations between cross-polarisers after regeneration of the blend, revealing discontinuous birefringence zones of cellulose separated by the xanthan phase (***Figure 11.c***).

After storage at 4°C, the cellulose/polysaccharides/NMMO mixtures with a constant concentration of cellulose of 10% in the solution and cellulose / polysaccharide ratios varying from 100 / 0 to 70 / 30 were further studied by means of DSC. Compared to pure NMMO solutions, the melting enthalpy and melting temperature (135 J/g and 74 °C for NMMO, respectively) are largely decreased in the case of cellulose/polysaccharides/NMMO mixtures, which is mainly caused by a decrease in the size of NMMO crystals. Cellulose and other polysaccharide chains actually hamper NMMO crystal formation, leading to lower melting enthalpies (***Figure 12***). As compared to pure cellulose/NMMO

mixtures, the presence of xanthan and carrageenan has a tendency to increase the melting enthalpy. It is possible that larger crystals are generated. An inverse phenomenon was observed for xylan. Thus, the globular morphology generated by cellulose/xylan blends impedes the formation of NMMO crystals more than the network morphology created in cellulose/xanthan or carrageenan blends.

Fibre production

Fibres in the form of multifilament yarn were manufactured from cellulose solutions in NaOH, NMMO and EMIMac using the wet spinning method [12, 20]. The composition of the polysaccharide blends was chosen taking into account the results obtained from solution studies. The textile-physical properties are decreased compared to those of unmodified fibre, with NMMO and EMIMac fibres having a slight advantage (***Table 4***). It should be remarked that the latter species was spun using the same technology and equipment, respectively. Differences in fibre properties are understood in terms of both the solvent and technology, which will be discussed in more detail in the next article prepared for publishing.

Initial trials of blend fibres from NaOH solutions were made with starch, CMC, as well as carrageenan and cellulose carbamate. The linear density planned for an individual filament was 2.2 dtex, respectively, for multifilament yarn of 630 dtex. In fact, the linear density obtained was in the range of 2.2 to 2.5 dtex. An increase in the content of the polysaccharide blend in the spinning dope resulted in a decrease in their mechanical properties. The only exception was the cellulose/CC fibre. Cellulose/polysaccharide fibres possess tenacities from 10 to 17 cN/tex and elongations of up to 12%, as measured for a single filament. Further fibres were produced with xanthan, gum tragacanth and LBG. Here, because of the reasons mentioned above, severe difficulties arose from the spinning. Further optimisation (temperature, the combining of solely dissolved cellulose and polysaccharide) succeeded in overcoming these problems, and fibres with a linear density from 2.5 to 6 dtex could be spun.

Whereas the production of fibres from NMMO could be achieved easily, spinning from EMIMac required more optimisation. Initial trials were conducted with xanthan, whose cellulose content had to be reduced to 5% in relation to cellulose because higher concentration ratios, e. g. 50/50 were not spinable. Even at a lower polysaccharide blend concentration, only fibres with a relative high linear density (ca. 60 dtex) could be spun when using LBG, guar gum, gum tragacanth and xylan. Furthermore, the spinning process was very unstable e.g. due to the higher elasticity of xanthan, the capillaries flipped back. Moreover, clumps in the jet holes caused permanent breaks of the filament. Further optimisation was made by increasing the dope temperature from 80 to 120 °C just before entrance into the spinneret. Despite the difficulties during spinning (including breaks), fibres with a titre near 2.5 dtex and a good tenacity typical for Lyocell fibres could be spun (***Table 5***). 1.5 kg of such fibres were produced in order to investigate their properties.

Table 5. *Mechanical properties of fibres; * yarn.*

Polysaccharide used in the blend	Tenacity [cN/tex]			Elongation [%]		
	Fibre type			Fibre type		
	NaOH	EMIMac	NMMO	NaOH	EMIMac	NMMO
Pure cellulose	17.1	46.5	44.2	11.0	14.7	13.1
Carrageenan	17.3		38.2	7.6		12.3
CC	17.0			9.4		
CMC	14.3*	42.7		3.5*	12.4	
Starch	13.4	36.7		9.0	11.2	
Xylan		42.8	37.1		13.2	13.5
LBG	12.9	43.6		17.2	12.9	
Guar gum		42.9			12.5	
Xanthan	14.2	43.8	41.3	11.1	13.4	11.6
Tragacanth gum	15.7	41.6	41.3	12.0	11.7	11.1

Table 6. *Sugar content of the blended polysaccharide.*

Polysaccharide sample	Arabinose, % rel.	Galactose, % rel.	Mannose, % rel.	Xylose, % rel.	Glucose, % rel.
Carrageenan	0	93.4	0.8	1.0	4.4
Cellulose carbamate	0.2	0.3	0	11.7	87.9
Gum tragacanth	47.1	12.2	0.2	17.4	19.0
LBG	0	20.3	76.9	0.2	2.4
Guar Gum	0	34.8	61.9	0.3	3.0
Xanthan	0.7	0.3	41.6	0.2	56.9
Xylan	0	0.4	0	93.4	1.3

Uptake studies

The goal of this analysis was to determine the uptake rations of various polysaccharides added to cellulose spinning dope during fibre production. Residue analysis was carried out by means of a special digestion method to measure the sugar compounds: arabinose, galactose, mannose, xylose and glucose in pure polysaccharide (***Table 6***) and blended fibre. Calculation of the uptake rations was based on the sugars, which were of a high proportion in the polysaccharide sample (except glucose), e. g. mannose was used for the calculation of xanthan and xylose for xylan uptake.

Although the database was reduced due to the sample amount required, some conclusions could be drawn. Compared to the theoretical values expected, based on the initial composition of the dope, the uptake rations amounted to between 10 and 92% (***Figure 13***.

The uptake rations of the fibres increase in the following order: NaOH – NMMO – EMIMac. The uptake depends more on the solvent than on the type of polysaccharide and technology. An exception is tragacanth gum, where recoveries are low compared to the other polysaccharides, irrespective of the solvent used. Moreover, both galactose and arabinose were detected in almost the same ratio. Even though NMMO and EMIMac fibres were spun on the same equipment, the latter favours higher amounts of the uptake of the other than cellulose polysaccharide. It can be concluded that the regeneration of fibres from NMMO is different, meaning that the hydrogen bond system between the cellulose chains and the blended polysaccharide is weaker than inside the cellulose skeleton. The re-

lease of blended polysaccharide from the skeleton might be easier.

In the case of CMC blended fibre, perchloric acid hydrolysis followed by anion exchange chromatography was applied. A general problem of CMC hydrolysis is the quite low yield of hydrolysis, which is not mentioned in most studies. The uptake rate was calculated from the most frequent structures: 6-O- and 2-O-carboxymethylglucose. In the present study the NaOH fibre possesses a higher uptake ration (11.7%) compared to the EMIMac fibre (5.2%).

For the determination of the starch uptake ration, enzymatic digestion with amylase degradation was applied prior to the analysis of the sugar. The enzyme might be partly inhibited by substituents, but the DS of the cationised starch is very low. For the starch sample a sugar yield of about 59% was measured. This value should be quite sensitive in order to detect starch in the fibre. However, after digestion, both the NaOH and EMIMac fibres did not show any significant uptake. Theoretically, it is possible that starch in the fibre body is physically not accessible to the enzyme. Otherwise, it is more likely that the uptake is extremely low.

Conclusions

The topics of this study cover the interactions of polysaccharides or their mixture in solutions, as well as the solid state after forming. 15 different polysaccharides were chosen to modify cellulose fibre with respect to its hydrophilicity, dyeability and surface charge. NMMO, EMIMac and NaOH are powerful solvents for both cellulose and cellulose/polysaccharide blends. Moreover, these solvents can be used to make solutions for subsequent fibre forming. Cellulose/polysaccharide blends can be prepared from NMMO and ionic liquids via Lyocell technology as well as from NaOH by a special wet-spinning process. As was shown, a variety of parameters have an impact on the performance of the blend fibres, mainly the type of spinning technology used, the nature of the solvent and the type of polysaccharide mixed with cellulose.

As shown by the dissolution screening experiments, CMC, CC, xylan, xanthan, guar gum, LBG and gum tragacanth gave good solubility in all three solvents (NaOH, NMMO and ionic liquid). Dissolution of chitosan species and chitin was impossible. Differences between the solvents occurred for MHEC, carrageenan, alginic acid, which were insoluble in EMIMac but soluble in the two others; starch and CMX, on the other hand, could not be dissolved in NMMO.

Investigations by rheology, DSC, microscopy and particle analysis showed that none of polysaccharides is able to produce a miscible blend with cellulose.
However, the spinning of fibres from all the solvents succeeded, even when using higher molar polysaccharides. The textile-physical properties are only slightly decreased compared to the unmodified fibre. It should be pointed out that the insertion of fine milled polysaccharides into the skeleton of cellulose is a crucial factor, as previously described for the modified Lyocell process with the application of both organic and inorganic compounds. Therefore, rather functional materials/polymers are more likely to produce the special features required for the fibres formed than the status of miscibility. Nevertheless, the morphology of blended solutions is of great interest in preventing the clogging of filters and controlling the final morphology and properties of the fibres regenerated.

The interest of such blends is the possibility of spinning composite fibres with the original properties. Further properties of the fibres produced in this study are a current topic of research and will be presented in the next paper, which is in preparation.

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